

Final Report

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Phase Equilibrium Investigations of Planetary Materials

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This grant provided funds to carry out phase equilibrium studies on the processes of chemical differentiation of the moon and the meteorite parent bodies, during their early evolutionary history. Several experimental studies examined processes that led to the formation of lunar ultramafic glasses. Phase equilibrium studies were carried out on selected low-Ti and high-Ti lunar ultramafic glass compositions to provide constraints on the depth range, temperature and processes of melt generation and/or assimilation. A second set of experiments examined the role of sulfide melts in core formation processes in the earth and terrestrial planets. The major results of each paper are discussed below and copies of the papers are attached as Appendix I.

A paper by Astrid Holzheid et al. (Appendix I, ms#1) investigated the textural equilibrium of olivine, silicate melt and metal sulfide melt under mantle conditions. The experiments were performed in a piston cylinder apparatus in capsules fabricated from single crystals of San Carlos olivine. We infer that thermal diffusion (Soret diffusion) of the metal sulfide melt occurred in the static temperature gradient of the run assembly. The dihedral angle between the iron alloy and olivine matrix varies from $< 70^\circ$ to $\sim 110^\circ$ depending on cation – sulfur abundance. Thus, the alloys form isolated melt pockets within the partly molten olivine matrix. This result implies that very large silicate melt fractions would be necessary to mobilize iron alloy melts in a partially molten mantle.

A paper by Linda Elkins et al. (Appendix I, ms#2) provides experimental constraints on the processes that led to the generation of the compositional variability observed in the Apollo 14 lunar ultramafic glasses. A multiple saturation point with olivine and orthopyroxene occurs at 1540°C and 2.2 GPa. Crystallization on the ol + opx saturation boundary involves 40 wt% ol and 60 wt% opx, and occurs over a 120°C interval before cpx appears at a reaction boundary. Crystallization/melting models are developed for the Apollo 14 glasses using these phase equilibrium constraints. We find that fractional crystallization alone cannot account for the observed variation in the major element abundance of the Apollo 14 green glasses. Assimilation is also necessary, in particular, to fit variations in TiO_2 , FeO , and Al_2O_3 . Both the 14A and 14B glasses show evidence of simultaneous high-Ti assimilation and elevated-pressure fractional crystallization. The depth is constrained to be shallower than the KREEP source region.

A paper with James Van Orman (Appendix I, ms#3) reports a set of experiments that were performed up to 1.8 GPa pressure on a composition from Snyder et al. (1992) of a model late stage magma ocean cumulate. At all pressures, the first melt is saturated with high-Ca pyroxene, ilmenite and quartz. Although TiO_2 contents are high and approach 13-14 wt. % TiO_2 , the compositions of the low degree partial melts of this model magma ocean cumulate do not resemble the compositions of any lunar high-Ti glasses. The CaO content is higher (> 9 wt. % CaO vs 6 to 7 wt. % for lunar high-Ti glasses) and Mg# ($\text{Mg\#} = 100 \cdot \text{Mg}/[\text{Mg} + \text{Fe}^{2+}]$ molar) is low (~ 15 vs ~ 50 in lunar high-Ti glasses). To extend the dissolution rate experiments on ilmenite in lunar magmas (Wagner and Grove, 1997) dissolution rates were measured for diopside and the melting kinetics of ilmenite + diopside bicrystals were examined. When these two minerals are in contact their melting rates are similar, because the kinetics of melting are controlled by the diffusion rates in the melt that is produced. Therefore, there are no kinetic effects on the melting process of an ilmenite and high-Ca pyroxene residue. Since this melt is very different in composition from that of a lunar ultramafic glass, the proposal of Wagner and Grove (1997) is not a likely process, unless ilmenite is separated from pyroxene as the cumulates sink into the underlying cumulates.

A paper with Astrid Holzheid (Appendix I, ms #4) investigates the solubility of sulfur in ultramafic silicate melts as a function of silicate melt composition, temperature and pressure to see what constraints it might place on the segregation of sulfide melt in planetary interiors. We find a negative pressure dependence for sulfur solubility. Therefore, a primitive magma that is S-saturated in its source, will become S-undersaturated as it ascends to shallower depth. The S content in a metallic liquid that is equilibrium with a magma ocean that contains ~ 200 ppm S (the Earth's bulk mantle S content) ranges from 5.5 to 12 wt. % S. This range of S values encompasses the amount of S that would be present in the outer core, if S were the light element. Thus, the Earth's proto-mantle could be in equilibrium with a core-forming metallic phase in terms of the preserved S abundance.

A paper by Linda Elkins-Tanton et al. (Appendix I, ms#5) examines the lunar magma ocean cumulate overturn hypothesis. A long-standing hypothesis is that the last fraction of the lunar magma ocean crystallized into a layer of dense, Ti-rich cumulate material at shallow depths (100 km) at the end of solidification of the lunar magma ocean. It has been suggested that the Ti-rich, dense cumulates subsequently sank deep into the moon because of gravitational instability. The paper reexamines several scenarios for the sinking of high-Ti cumulate materials. We find that sinking of these cumulates is unlikely because the temperature under which the cumulates solidify is low and viscosity under these conditions is very high. However, it is possible that high-Ti cumulates mixed with olivine in substantial amounts would have low enough viscosities to sink as solids. It is also possible that remelted high-Ti cumulates would be negatively buoyant and sink as liquids, percolating downward through the lunar mantle and beginning to crystallize ilmenite at 200 km depth, making a hybrid, heterogeneous cumulate.

Appendix I

Publications resulting from Grant NAG5-9525

1. A. Holzheid, M.D. Schmitz and T. L. Grove (2000) Textural equilibria of iron sulfide liquids in partly molten silicate aggregates and their relevance to core formation scenarios. *J. Geophys. Res.* 105, p. 13555-13567.
2. L.T. Elkins, V.A. Fernandes, J.W. Delano and T.L. Grove (2000) Origin of lunar ultramafic green glasses: Constraints from phase equilibrium studies. *Geochim Cosmochim Acta* 64, p. 2339-2350.
3. J.A. Van Orman and T.L. Grove (2000) Origin of lunar high-Ti ultramafic glasses: Constraints from phase relations and dissolution kinetics of clinopyroxene-ilmenite cumulates. *Meteoritics Planet. Sci.* 35, p. 783-794.
4. A. Holzheid and T.L. Grove (2002) Sulfur saturation limits in silicate melts and their implications for core formation scenarios for terrestrial planets. *Amer. Mineral.* 87. P. 227 – 237.
5. L.T. Elkins-Tanton, J.A. Van Orman, B.H. Hager and T.L. Grove (2002) Reexamination of the lunar magma ocean cumulate overturn hypothesis: melting or mixing is required. *Earth Planet. Sci. Lett.* 196, p. 239-249.